Extraordinary Responsive Magnetic Rare Earth Materials

Complex and Magnetocaloric Materials

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For FY2003-2005 -

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OUTPUT SUMMARY – FY2003-2005

Invited Conference Presentations	14
Other Invited Presentations	27
Contributed Presentations	31
Journal Papers	44
Conference Papers	4

ABSTRACT AND BACKGROUND

Research is focused on systematic experimental and theoretical studies of the unique magnetic-martensitic phase transformation in R_5T_4 materials (where R is Gd and other rare earths and T is a main group-IV element Si, Ge, or Sn, and in some cases, a certain amount of Ga or Sb substituting for Si, Ge and/or Sn) to achieve understanding of the underlying electronic structure and the microscopic interactions bringing about extremely strong coupling of the magnetic moments with the lattice. Another goal is the development and validation of a phenomenological-based model of the magnetic-martensitic transformation, which will provide fundamental guidance for the discovery of novel material systems exhibiting extremely large magnetocaloric, magnetostrictive, and magnetoresistance responses to small changes of magnetic field, temperature, and pressure.

The distinctiveness of the R_5T_4 series can be linked to crystallographic low-dimensionality of its members. Regardless of x, all R_5T_4 compounds are natural multi-layers, where flat sheets of tightly bound R and T atoms are sandwiched between two densely populated

rippled sheets of R and capped by two planar sheets loosely occupied by the T atoms. These five-sheet assemblies are less than one nanometer-thick, forming remarkably stable two-dimensional slabs, the stacking of which varies with x and defines the physical properties of compounds from the R_5T_4 series. For example, for R = Gd and T = (Si_xGe_{4-x}) when x ≥ 2.3, the Gd_5T_4 alloys order ferromagnetically *via* conventional second-order transformations with the T_C gradually lowering from 336 K for x = 4 to 306 K for x = 2.3. Further increase of the Ge concentration, however, has a drastic effect on both the structural and physical properties of the parent silicide. Thus, in compounds with x < 2.1, the ferromagnetic ordering/disordering couples with a martensitic phase transformation. The cooperative action of both the magnetic and structural transitions results in the giant magnetocaloric and magnetoresistance effects, colossal magnetostriction and many anomalies of the electronic transport behavior.

This research is being carried out by a multidisciplinary group of scientists from the Materials and Engineering Physics, Condensed Matter Physics, and Materials Chemistry and Biomolecular Materials Programs of the Ames Laboratory. Numerous collaborations with leading research groups in the US and internationally have been established and are continuously expanding. With such a group, a number of different approaches, both experimental and theoretical, are being brought to bear on these extraordinary materials in order to understand their basic nature.

TECHNICAL HIGHLIGHTS

- Synthesized by the tri-arc method $R_5Si_xGe_{4-x}$ crystals, with R = Gd, Tb and Er, that do not contain the macro-cracking or W impurities commonly encountered in Bridgman grown crystals. Sizable crystals of $Tb_5Si_xGe_{4-x}$ compounds have been prepared for neutron scattering studies and magnetic property characterization.
- *In situ* X-ray diffraction studies of the $Gd_5Si_xGe_{4-x}$ alloys with $1.72 \leq x \leq \sim 2$ revealed that the low temperature (~220 K to ~280 K) martensitic transformations are rapid, complete and reversible when they are coupled with the ferromagnetic ordering on cooling and disordering on heating. The same martensitic phase changes that occur above ~500 K are slow, incomplete and irreversible in the paramagnetic state. Magnetic interactions and the magnetic exchange energy, therefore, play a crucial role in the phase transition processes in the $Gd_5Si_{4-x}Ge_x$ system.
- At 220 K, a transformation from the orthorhombic Gd_5Si_4-type material to a monoclinically distorted $Gd_5Si_2Ge_2$-type structure is observed in pure Er_5Si_4. The compound orders ferromagnetically *via* a second-order phase transformation at ~30 K. Magnetic fields higher than 70 kOe are required to trigger a structural transition of the monoclinic Er_5Si_4 to presumably the orthorhombic polymorph in the ferromagnetic state. The giant magnetocaloric effect (MCE), hence, is observed in Er_5Si_4 only when the magnetic field exceeds 70 kOe. This result is consistent with our theory that elastic contributions may significantly enhance the MCE when compared to the contributions from only a spin system.
- $Gd_5Si_2Ge_2$ shows a high-temperature monoclinic-to-orthorhombic ($\beta \rightarrow \gamma$) transition, which is not coupled with magnetic ordering and is opposite to the low-temperature magnetic-martensitic transition with respect to the symmetry sequence. *In situ* high-temperature studies revealed that the $\beta \rightarrow \gamma$ phase transition in $Gd_5Si_2Ge_2$, which occurs at 573-593 K, is driven by an increase in the lattice entropy (a higher degeneracy of the electronic and vibrational states due to the higher symmetry), but not by the configurational entropy (fully statistical, macroscopic distribution of the Si and Ge atoms). This suggests that the structure of the low-temperature, ferromagnetic, orthorhombic α-phase is dictated by a strong magnetic exchange coupling, which overcomes the unfavorable entropy contribution even near room temperature.

- Cooling of the two-phase (β + γ) single crystals of $Gd_5Si_2Ge_2$ into a single-phase α region followed by subsequent re-heating to room temperature revealed "structural memory". Specifically, the crystals "remember" structural details of the two phases at room temperature. The two-phase (β + γ) single crystals also reveal "magnetic memory", existing in parallel with the structural memory. These structural and magnetic studies point to the coexistence of structurally and magnetically different polymorphs of the same compound at some temperatures.
- The largest magnetocaloric effect (MCE) is observed when a material orders magnetically *via* a first-order phase transformation. The fundamental relationships between the two characteristics of the MCE (i.e. the isothermal entropy change and the adiabatic temperature change) and the most basic thermodynamic property of solids (i.e., the heat capacity at constant pressure as a function of temperature in constant magnetic fields) have been derived theoretically and validated by comparing with the experiment.
- A one-of-a-kind X-ray powder diffraction system based on a Rigaku rotating anode powder diffractometer coupled with a helium flow cryostat (temperature range from 2.2 K to 315 K) and a 40 kOe split-coil superconducting magnet has been fully instrumented, tested and calibrated. The instrument facilitates the collection of exceptionally high quality Rietveld-ready X-ray diffraction data and enables direct observation of the influence of the magnetic field and temperature on the atomic structure of R_5T_4 compounds and other materials.
- The structural transformations and the imaging of the shifting atoms in Gd_5Ge_4, $Gd_5Si_{0.5}Ge_{3.5}$, and Er_5Si_4 compounds were mapped as a function of magnetic field at constant temperature, and as a function of temperature at constant magnetic field resulting in precise structural diagrams in temperature – magnetic field coordinates.
- The anisotropy of the magnetic properties and possible details of both the antiferromagnetic and ferromagnetic structures of Gd_5Ge_4 have been identified from single crystal magnetic measurements.
- Identified extended regions where Gd_5Ge_4, $Gd_5Si_{0.5}Ge_{3.5}$, and Er_5Si_4 lose homogeneity and become magnetically (the first two) and structurally (all three) inhomogeneous. These states are somewhat similar to the phase separated states observed in the colossal magnetoresistive manganites, in which different polymorphs are usually related *via* Jan Teller distortions. Surprisingly, only 93% of Gd_5Ge_4 transforms to the ferromagnetic phase by applying magnetic field as high as 35 kOe. Similarly, 5 to 7 % of $Gd_5Si_{0.5}Ge_{3.5}$ remains untransformed by varying either or both the temperature and magnetic field. For Er_5Si_4, nearly 20 % of the monoclinic phase is still retained even at 5 K, i.e. more than 200 K below the temperature of the orthorhombic to monoclinic structural transformation.
- The magnetic structures of $Tb_5Ge_{2.2}Si_{1.8}$ and $Tb_5Ge_{2.5}Si_{1.5}$ compounds, determined from elastic neutron scattering experiments, can be described by a single model in the magnetic space group Pnm'a' above 75 K. Below 75 K, a mixed ferromagnetic state with one structure having a net ferromagnetic component parallel to the *a*-axis and a second structure with a net ferromagnetic moment along the *c*-axis were needed to describe the neutron diffraction pattern. Magnetic moments of Tb are fully developed.
- X-ray magnetic resonant scattering data indicate that the microscopic antiferromagnetic structure of Gd_5Ge_4 is close to our predictions from magnetization measurements of single crystals. Magnetic moments of Gd are fully developed.
- Scanning electron microscopic (SEM) and transmission electron microscopic (TEM) experiments on single crystals of $Gd_5Si_xGe_{4-x}$ have identified the presence of second-phase plates of stoichiometry Gd_5SiGe_2 (i.e. 5:3 composition). These plates are extremely

thin and often extend over hundreds of microns. The omnipresence of these structures in the $R_5Si_xGe_{4-x}$ systems raises several important fundamental questions as to the mechanism whereby such a structure can form and grow. Our results indicate that these second-phase plates form in the solid state via a displacive-diffusion mechanism during cooling.

- We have performed fully relativistic, spin-polarized electronic structure calculations using the linearized augmented plane wave method, modified to take into account the very strong on-site Coulomb correlation of the 4*f* electrons (the LSDA+U approach). Our calculations yielded about 7.5 Bohr magnetons per Gd atom, similar to pure hcp Gd metal. These predictions have been correlated with specifically designed experiments to determine the low temperature saturated magnetic moment in single crystals of $Gd_5Si_2Ge_2$. Experimental value of 7.31 ± 0.04 Bohr magnetons per Gd atom allowed us to draw conclusions about the induced 5d moments, which are key to the electronic structure.
- We applied linear-muffin-tin-orbital LMTO method, including LSDA+U corrections, for description of the 4*f* states of Gd. The structural stability of the orthorhombic phase is mainly related to the formation of interslab T-T Ge(Si) bonds. The decrease of splitting between bonding and antibonding p-states of the Ge(Si) atoms directly affects the exchange in the monoclinic phase. A qualitative analysis of the free energy for both phases shows that the first-order phase transition from the ferromagnetic orthorhombic phase to the paramagnetic monoclinic phase can be described in our approach. The LSDA+U description of 4*f* Gd states results in larger values of magnetic exchange parameters compared with LSDA results. This correction yields the calculated magneto-structural transformation temperature of 200 K, which is close to 270 K observed experimentally. The calculated values of the magnetocaloric effect and the latent heat of the magneto-structural phase transition are in good agreement with experiment.
- Motivated by experimental measurements of the magnetotransport properties of a single crystal, we computed the magnetoresistance of $Gd_5Si_2Ge_2$. Our approach revealed a complex behavior of the conductivity tensor with a rather strong anisotropy. The anisotropy is induced by the layered structure of $Gd_5Si_2Ge_2$. The main contribution to the conductivity of the compound comes from *d*-states of Gd, which are modified through the phase transformation. The main source of the giant magnetoresistance is a structural transformation coupled with the magnetic ordering-disordering process.

INTERACTIONS WITH OTHER PROJECTS AND PROGRAMS

This project represents a broad experimental and theoretical effort concentrated on materials with first order magnetic-martensitic phase transformations. In addition to intimate collaborations between investigators from the three major Programs at the Ames Laboratory, numerous outside collaborations, both nationally and internationally, have been established and new ones are continuously being developed. Research results obtained in this project are also of interest to the studies being carried out in other focus areas within the Program, especially the Magnetism focus area and some aspects of the Condensed Matter Physics Program.

SELECTED PUBLICATIONS

V.K. Pecharsky, A.P. Holm, K.A. Gschneidner, Jr., and R. Rink, "Massive Magnetic-Field-Induced Structural Transformation in Gd_5Ge_4 and Nature of the Giant Magnetocaloric Effect," *Phys. Rev. Lett.*, **91**, 197204/1 - 4 (2003).

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K.A. Gschneidner, Jr., V.K. Pecharsky, and A.O. Tsokol, "Recent Developments in Magnetocaloric Materials," *Rep. Progr. Phys.,* **68**, 1479 (2005).

L. Tan, A. Kreyssig, J.W. Kim, A.I. Goldman, R.J. McQueeney, D. Wermeille, B. Sieve, T.A. Lograsso, D.L. Schlagel, S.L. Budko, V.K. Pecharsky, and K.A. Gschneidner, Jr., "The Magnetic Structure of Gd_5Ge_4," *Phys. Rev. B.*, **71**, 214408/1 – 6 (2005).

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O. Ugurlu, L.S. Chumbley, D.L. Schlagel, T.A. Lograsso, and A.O. Tsokol, "Identification of thin plates seen in $R_5(Si_xGe_{1-x})_4$ alloys, where R is Gd, Tb, Dy, and Er," *Scr. Mater.,* **53**, 373 (2005).

The Nature of the Distinctive Microscopic Features in $R_5Si_xGe_{4-x}$ Materials

Personnel: L.S. Chumbley (PI), T. Lograsso (PI), D.L. Schlagel (Assistant Scientist), A.O. Tsokol (Assistant Scientist), and O. Ugurlu (Grad. Student)

Scope:

$R_5Si_xGe_{4-x}$ alloys, where R is Gd, Tb, Dy and Er, have been examined using a full array of electron microscopy techniques. In addition to the major matrix phase, a second phase in the shape of thin plates has been observed and studied. Energy dispersive spectroscopy shows that this secondary phase apparently has a stoichiometry of $R_5Si_xGe_{3-x}$. The orientation relationship between the hexagonal plates (p) and the monoclinic or orthorhombic matrix (m) is described as $[1\ 0\ \bar{1}\ 0](1\ \bar{2}\ 1\ 1)_p//[0\ 1\ 0](1\ 0\ \bar{2})_m$. It appears that the second-phase plates form in solid state via a displacive-diffusional mechanism during cooling.

Research Highlights:

This study focuses on the appearance of linear features observed by Szade, Skorek and Winiarski in 1999 on the surface of a few $Gd_5Si_xGe_{4-x}$ alloys, also found in *all* R_5T_4 compounds regardless of the processing path of the material. Elucidating the identity and origin of these features is central to more fully understanding the structure-property relationships of responsive magnetic rare earth materials. Our examination of a series of $R_5Si_xGe_{4-x}$ compounds (including R = Gd, Tb, Dy, and Er) with sample compositions covering the range from the Ge-rich Sm_5Ge_4-type orthorhombic structure through the intermediate $Gd_5Si_2Ge_2$-type monoclinic structure to the Si-rich Gd_5Si_4-type orthorhombic structure, has consistently revealed the presence of a second phase with stoichiometry close to $R_5Si_xGe_{3-x}$ (i.e., this phase contains ~62.5 at.% of the lanthanide element compared to the ~55.5 at.% of the same in the $R_5Si_xGe_{4-x}$ matrix). This phase appears as extremely thin plates in all samples, independent of whether the crystal structure is orthorhombic (either the Sm_5Ge_4- or Gd_5Si_4-type) or monoclinic (the $Gd_5Si_2Ge_2$-type). The platelets are crystallographically coupled to the matrix crystal structure as illustrated in Fig. 1a, similar to what is expected for a Widmanstätten structure. The plates form in the solid state upon cooling, even at relatively high cooling rates seen in the arc-melted specimens. The three-dimensional relationships of the plates are clearly displayed in the digitally reconstructed image of a single crystal of $Gd_5Si_2Ge_2$ shown in Fig. 1b, and also, in Fig. 1c, which depicts a scanning electron microscopy (SEM) view taken at the edge formed by two polished faces of a single crystal. When examined along [100] and [001], the linear features lie nearly parallel to the [010]; whereas, when viewed from the [010] the linear features lie in two directions with an 80° angle between them. They are aligned ±40° from the [001] and ±50° from the [100] in the crystal. The bright field (BF) transmission electron microscopy (TEM) image shown in Fig. 1d, taken with the electron beam perpendicular to [010], supports the SEM results.

Selected area diffraction (SAD) patterns and high resolution TEM (HRTEM) were used to elucidate the crystal structure, orientation relationship and transformation mechanism for the formation of this phase. The plates possess a hexagonal crystal structure similar to that reported for the lanthanide R_5Si_3 and R_5Ge_3 compounds. The orientation relationship was determined as $[1\ 0\ \bar{1}\ 0](1\ \bar{2}\ 1\ 1)_p//[0\ 1\ 0](1\ 0\ \bar{2})_m$ from the diffraction patterns and stereographic projections. This orientation relationship is illustrated in Fig. 1e, which contains diffraction patterns from both the matrix and precipitate phases. It is apparent in this image that a 7° rotation exists between the phases; such an observation is a critical point in determination of the formation mechanism of this phase. Figure 1f shows an HRTEM image, which demonstrates the 7° rotation as well as edge-to-edge plane matching between $(0001)_p$ and $(100)_m$.

These observations are consistent with an invariant line strain, which we hypothesize as being present in the formation of these thin-plates. Similar observations have been reported by Dahmen and Zhang, where mechanisms for a displacive mode of transformation were proposed in simple systems. Using the Δg theory proposed by Zhang, the habit planes of the thin-plates were calculated as (22 0 19) and ($\bar{2}\bar{2}$ 0 19).

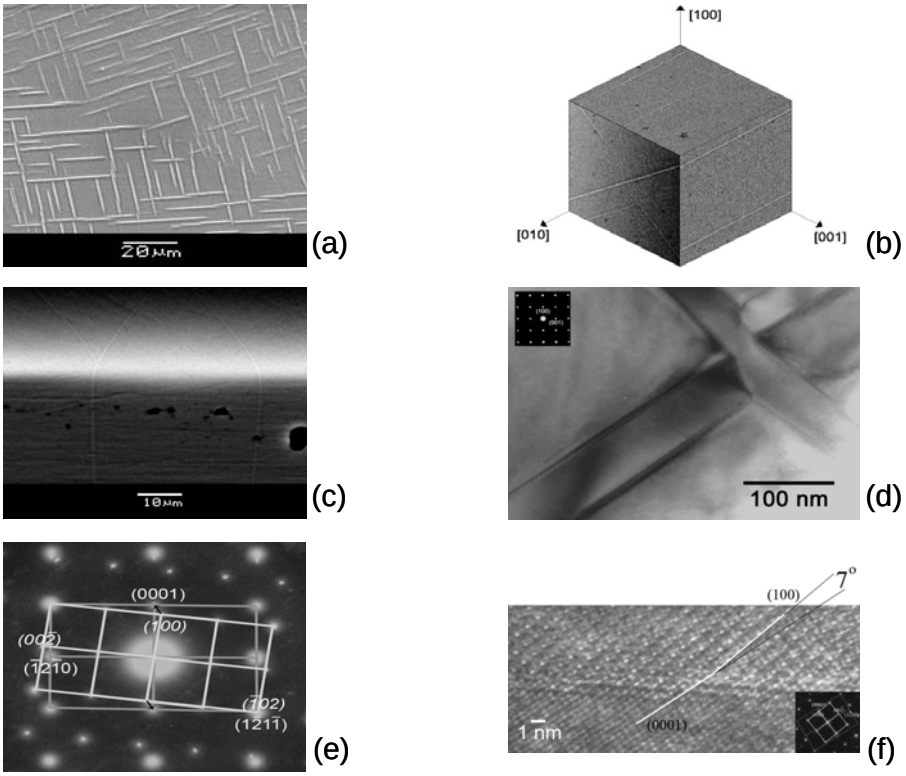


Fig. 1 Electron microscopy images of a $Gd_5Si_2Ge_2$ single crystal. Surface SEM micrograph (a); digital, three-dimensional composite of the crystal with platelets (b); SEM view of the edge formed by two polished faces (c); TEM image with the electron beam perpendicular to [010] (d); Orientational relationship between reciprocal lattices matrix and the platelets (e); HRTEM image demonstrating the 7° rotation and edge-to-edge plane matching between $(0001)_{plate}$ and $(100)_{matrix}$ (f).

Impact:

This work represents the first quantitative assessment of the secondary, plate-like $R_5Si_xGe_{3-x}$ phase in $R_5(Si_xGe_{1-x})_4$ alloys. Based on the observed invariant line strain, the formation of this phase even at high cooling rates and its difference in stoichiometry compared to that of the matrix, it is inferred that its formation mechanism likely involves both displacive and diffusional components. Earlier solid-solid interface studies of displacive-diffusion transformations have been carried out on simple cubic or hexagonal systems. If the presently proposed mechanism can be confirmed, it will represent the first ever report of such a dual-nature solid-solid transformation in an extremely complex system.

Future Work:

Details of the transformation mechanism are still under investigation. Superior HRTEM images need to be taken and simulated for a better understanding of the mechanism. In addition, we are trying to determine the temperature and composition range where these thin-plates form. This may require a major change to the currently available phase diagrams. Another caveat involves the apparent absence, or at least our inability to detect Gd-poor regions that are required to conserve mass. This uncertainty may require development of a new model other than the appearance of the 5:3 phase, for example involving an unusual twinning of the 5:4 crystallites, in order to explain the persistence of such distinctive microscopic features.

Interactions:

Close collaboration with V.K. Pecharsky and K.A. Gschneidner, Jr. Technical discussions with all PI's within the Complex and Magnetocaloric Materials project. A collaboration with Prof. B. Muddle of Monash University, who is an expert in solid/solid transformations, has recently commenced.

Synthesis of $R_5Si_xGe_{4-x}$ Single Crystals

Personnel: T.A. Lograsso (PI), D.L. Schlagel (Assistant Scientist), A.O. Tsokol (Assistant Scientist), and J.A. Sampaio (Postdoc)

Scope:

This effort focuses on developing synthesis and processing methods for the preparation of $R_5Si_xGe_{4-x}$ compounds free from microstructural and macrostructural defects, specifically, on Bridgman and crucible-less tri-arc crystal pulling. The $R_5Si_xGe_{4-x}$ alloys, which exhibit the giant magnetocaloric effect, hold promise for a future transition from vapor compression-based cooling to energy-saving magnetic refrigeration. In addition to the extraordinary strong magnetocaloric effects, potent magnetostrictive and magnetoresistive responses are displayed by many members of this family of materials. The availability of single crystals is, therefore, critical in order to understand the fundamentals of the coupled magneto/structural transitions that are believed to be responsible for such a combination of unusual behaviors in these complex compounds.

Research Highlights:

Both the Bridgman and tri-arc crystal pulling techniques have been shown to be viable methods for growing single crystals of $R_5Si_xGe_{4-x}$ alloys; however, each technique offers a unique set of advantages and disadvantages. Thus, we examine the two techniques using the $Gd_5Si_2Ge_2$ stoichiometry. In the Bridgman growth, the tungsten crucible was found to be chemically inert with respect to Gd, Si, and Ge but did have limited solubility in liquid $Gd_5Si_2Ge_2$, resulting in the precipitation of pure tungsten throughout the bulk crystal. Although tungsten precipitates were found to have little to no effect on the magnetic properties of these materials, upon cooling the crystal was severely cracked due to the mismatch of thermal expansion between $Gd_5Si_2Ge_2$ and the crucible (Fig. 1, top), thus limiting specimen size and complicating orientations. Overall, the bulk crystal solidified in the monoclinic structure and a slight increase in Si content and decrease in Ge content as the growth proceeded was observed. While generally smaller in diameter, crystals prepared by the tri-arc method (Fig. 1, bottom) do not fracture during cooling from thermal mismatch nor do they contain impurity phases attributable to a crucible, as stated above and they have been shown to be more phase pure than Bridgman grown samples. However, for tri-arc grown crystals, there is a slight increase in Si content and decrease in Ge content as the growth proceeds.

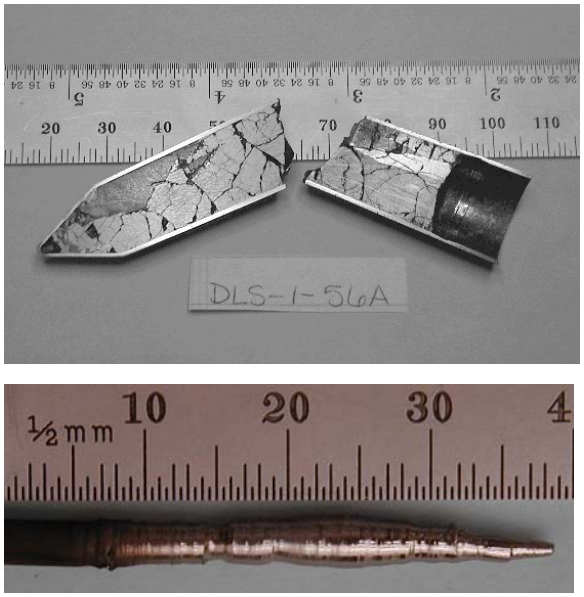


Fig. 1 $Gd_5Si_2Ge_2$ single crystals grown using the Bridgman method in a tungsten crucible (top) and the tri-arc crystal pulling method (bottom).

Differential scanning calorimetry (DSC) was found to be the accurate method for characterizing the ingots for phase purity, chemical composition and transition temperature values. Samples were taken from along the length of both crystals for characterization. Figure 2 shows a representative DSC curve of a $Gd_5Si_2Ge_2$ crystal sample showing two consecutive cycles. The main feature on cooling is due to the low temperature reversible monoclinic (M) to orthorhombic (OI) transition (as confirmed by X-ray diffraction) where the observed giant magnetocaloric effect is the result of a coupled magnetic and

structural transition. The reverse transition can be seen on heating. The double-arrowed line points out the Curie temperature (T_c) of the OI phase, a small amount of which likely formed during the crystal growth process either as: i) the crystal passed through the temperature range 623 K – 873 K in which M is irreversibly transformed to OI, or ii) by presence of an excess of Si shifting the composition to the OI region of the phase diagram, or iii) the OI phase may be stabilized by the presence of oxygen. The orthorhombic OI phase, regardless of how it was formed, persists even after cycling through the low temperature transition, and it remains an undesired, inactive constituent of the system. Because of the possibility of an irreversible transformation at high temperatures, the DSC scans were kept below the temperature range where such irreversible transformations occur. DSC results in tandem with XRD analyses showed that the Bridgman ingot contains both the M and OI phases. From microstructural analysis, the occurrence of the second phase was found to be random, precipitating in different regions of the ingot. Two tri-arc ingots were fully characterized and one ingot contained a small amount of the OI phase, while the second was found to be entirely single phase M.

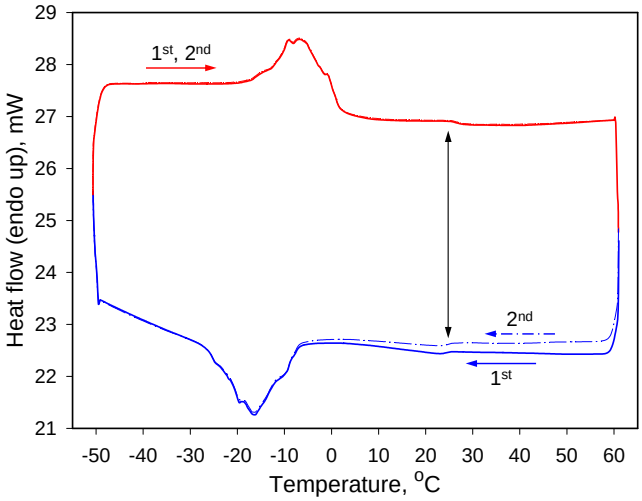


Fig. 2 DSC traces of a $Gd_5Si_2Ge_2$ sample. Scan rate was 10°C/min. Two consecutive cycles show reproducibility and reversibility of transitions. Main features are OI → M on heating and M → OI on cooling. The double-headed vertical arrow points to the T_c of the OI phase.

Impact:

The high quality of $R_5Si_xGe_{4-x}$ crystals prepared using the tri-arc crystal pulling method facilitate experimental investigations targeting the understanding of the mechanisms leading to coupled magnetostructural phase transformations. The availability of high-quality well-characterized single crystals has allowed a number of focused investigations on the anisotropic nature of magnetoresponsive and elastic properties, as well as field and pressure effects on the magnetostructural transformation of $Gd_5Si_xGe_{4-x}$ compounds. X-ray resonance magnetic scattering has been used to determine the magnetic structure of Gd_5Ge_4. Furthermore, large single crystals of several $Tb_5Si_xGe_{4-x}$ compounds have been prepared for neutron scattering studies, leading to the first determinations of magnetic structures based on single crystal data. Numerous other experimental investigations of the single crystals are in progress.

Future Work:

We will extend the synthesis to include other rare earth elements where certain alloys have exhibited unusual properties or behavior (e.g., Er_5Si_4, where the magnetic field apparently affects the crystallographic-only transformation well into the paramagnetic region, nearly 200 K above its magnetic ordering temperature). Accordingly, we will explore other elemental substitutions (Ga, Sb for Si/Ge) to vary the electronic concentration of these compounds in order to study how changing the electronic structure affects the unique properties of the $R_5Si_xGe_{4-x}$ alloys. We will continue to strive to optimize the tri-arc synthesis method for $R_5Si_xGe_{4-x}$ alloys in order to improve reproducibility, size and yield of high purity single crystals.

Interactions:

This work is in collaboration with all the PI's, Contributing PI's, Assistant Scientists, Outside Collaborators, Postdocs and Graduate Students in the Complex and Magnetocaloric Materials effort.

Effects of Chemical Substitutions on Structure, Bonding and Properties in R_5T_4 Materials

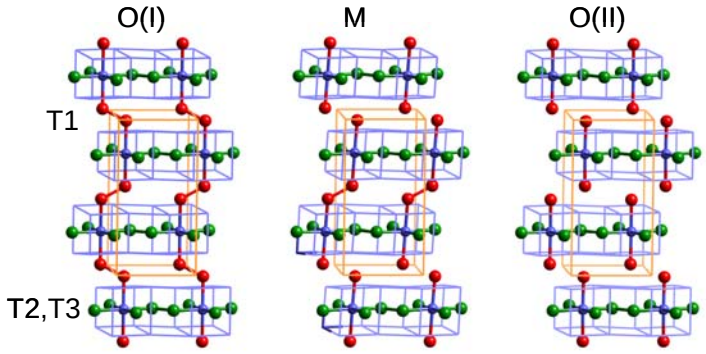
Personnel: G.J. Miller (PI), Y. Mozharivskyj (Post Doctoral Associate), S. McWhorter (Graduate Student), S. Misra (Graduate Student), and E. Poweleit (Undergraduate Student)

Scope:

This research effort involves three different themes: (1) synthesis and structural characterization of new compounds related to the $Gd_5Si_xGe_{4-x}$ system obtained by substituting nonmagnetic trivalent elements for Gd to identify specific magnetic interactions in the parent system, or by replacing Si or Ge atoms with other main group elements to study the effects of changing the number of valence electrons per formula unit; (2) temperature-dependent, single crystal diffraction of various $R_5T_xT'_{4-x}$ samples (R = rare-earth elements; T, T′ = main group elements) to study interrelationships between possible structural and magnetic transitions; and (3) electronic structure calculations within both the local density and local spin density approximations to examine the nature of interatomic interactions among the different structure types and to study the relationship between magnetic order and chemical bonding.

Research Highlights:

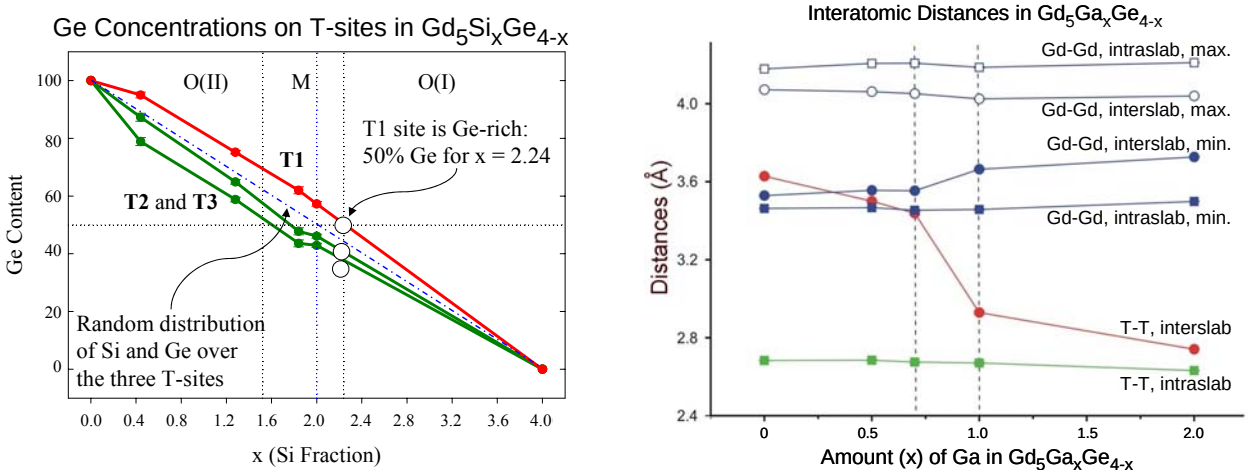
The complexity and versatility of the R_5T_4-type giant magnetocaloric materials allows numerous chemical substitutions to study various types of perturbations. The parent orthorhombic crystal structures for Gd_5Si_4 and Gd_5Ge_4 each contain three distinct R atom sites and three distinct T atom sites. We explore these substitutions within the systems using experiment and theory, ultimately aiming for experiments guided by theory, and have achieved the following results:



(a) *Elucidating the site preferences for different T and T′ elements in the R_5T_4-type structures*: Through single crystal X-ray diffraction and electronic structure calculations, we are furthering the understanding of how different elements distribute themselves throughout these complex structures, and their influence on structural and physical properties. In $Gd_5Si_xGe_{4-x}$, a single crystal study shows that Ge atoms have a slight preference for the T1 sites (red colored in the figure above, also see the figure on the left on the next page) that are responsible for the T-T bonds between the $[Gd_5T_4]$ slabs. Preliminary calculations of the total valence electron energy indicate that this "coloring" of the T sites correlates with the observed structural and phase behavior. We have also studied $Gd_5Sn_xGe_{4-x}$ and $Gd_5Sn_xSi_{4-x}$, which allow comparisons between sizes and electronegativities of T and T′ atoms while keeping the number of valence electrons constant. In both cases, Sn atoms prefer the T1 sites, which suggests that size factors are more important than electronegativity differences.

(b) *Effects of varying valence electron concentration on structure and properties*: $Gd_5Ga_xGe_{4-x}$ exists for $x \leq 2.1$, and x=2.1 gives the minimum number of valence electrons at 28.8 electrons per formula unit. For $0.5 < x < 1.0$, the room temperature structure changes from the Sm_5Ge_4-type [O(II), no T-T bonds between slabs] to the Gd_5Si_4-type [O(I), covalent-like T-T bonds between all slabs]. This effect correlates with depopulating T-T antibonding states as the valence electron concentration drops (see the figure on the right, next page). Furthermore, low temperature X-ray diffraction studies of $Gd_5Ga_{0.5}Ge_{3.5}$ show

O(II)–monoclinic (M)–O(I) structural changes on decreasing temperature, which correlates with magnetic ordering. Although Ga and Ge are indistinguishable by X-ray diffraction, other examples indicate that R_5T_4 systems exist for concentrations between ~29 and ~32 valence electrons per formula unit.



(c) *Effects of substituting Y for Gd in Gd_5Ge_4*: To investigate the relationship between exchange interactions and structure, we have prepared a series of $Y_5Gd_{5-z}Si_xGe_{4-x}$ alloys. For $Y_zGd_{5-z}Si_4$ and $Y_zGd_{5-z}Ge_4$, increasing z leads to dilution of the localized magnetic moments on Gd while the unit cell volumes decrease. Y_4GdGe_4 gives a new monoclinic structure type for the R_5T_4 system. At this stage, we have single crystal diffraction results and are studying magnetic properties of this range of compositions. Other research activities include (i) identifying a decoupling of the structural and magnetic transitions in Er_5Si_4 and (ii) thoroughly characterizing the high-temperature structural transition at 590 K in $Gd_5Si_2Ge_2$.

Impact:

Our efforts focus on chemical substitutions in the $R_5(T,T')_4$ systems to understand how perturbations to the crystal and electronic structure elicit responses to this fascinating and complex pseudobinary system. Our work emphasizes the relationships between chemistry, bonding and properties of these systems. At this point, we have a sound picture of the relationships between structure and valence electron concentration as well as on factors influencing atomic distributions. We still need to elucidate the interrelationships between different magnetic orderings and chemical bonding within the main group element and rare earth metal substructures as well as between them.

Future Work:

Through a combination of theoretical calculations, temperature-dependent single crystal X-ray diffraction and magnetization measurements, we plan to expand the scope of our efforts to provide a unified picture of the structural and magnetic phase diagrams in the R_5T_4 systems. Specific efforts will focus on (a) high temperature single crystal studies of Gd_5GaGe_3, which shows T-T bonds between the $[Gd_5T_4]$ slabs at room temperature; (b) to explore $Yb_5Si_xGe_{4-x}$ systems because Yb shows mixed valence behavior in all range of concentrations – such mixed valency may lead to interesting structural effects as a function of composition and temperature; (c) variable temperature crystallography and magnetization studies of $Y_zGd_{5-z}Ge_4$ and $Y_zGd_{5-z}Si_4$ to explore how the average exchange interaction and chemical structure varies with composition; and (d) exploring mixed rare-earth systems, e.g., $Nd_zEr_{5-z}Ge_4$ to further investigate the nature of orbital and magnetic interactions in rare-earth systems.

Interactions:

Experimental: V.K. Pecharsky, K.A. Gschneidner, Jr. (magnetic measurements, synthesis)
Theoretical: V.P. Antropov (spin polarized electronic structure calculations)

Magnetostriction and Magnetocrystalline Anisotropy of $Gd_5Si_xGe_{4-x}$ and $Tb_5Si_xGe_{4-x}$

Personnel: D.C. Jiles (PI), J.E. Snyder (PI), M. Han (Graduate Student), A.P. Ring (Graduate Student), J.S. Leib (Graduate Student), J.A. Paulsen (Graduate Student), and H. Ziegler (Undergraduate Student)

Scope:

The objective of this research is to conduct systematic experimental studies of the magnetoelastic properties of rare earth compounds of the type $Gd_5Si_xGe_{4-x}$ and $Tb_5Si_xGe_{4-x}$ in order to achieve understanding of the nature of the extremely strong magnetoelastic coupling of the magnetic moments with the lattice, and its influence on many intriguing behaviors of these materials. Magnetoelasticity is of specific interest because the giant magnetocaloric effect, giant magnetostriction, and giant magnetoresistance effects all occur in the neighborhood of a first-order magnetostructural phase transformation. A second objective is to develop and validate a phenomenological model of the transformation, which will allow the design of novel material systems exhibiting extremely large responses to small changes in magnetic field and temperature.

Research Highlights:

We have performed thermal expansion and magnetostriction measurements of a $Gd_5Si_2Ge_2$ single crystal along 3 principal crystallographic directions. Thermal expansion, measured with a series of different applied fields, showed that the magnetostructural phase transition temperature (T_c) depends strongly on the magnetic field, increasing by ~5 K/T. This brings about the giant magnetostriction at temperatures higher than the zero-field T_c. For example, and as seen in Fig. 1a, starting above the zero-field transition temperature, then applying a magnetic field can trigger the magnetostructural phase transition and its associated giant strain (greater than 10^{-3}). On the other hand, magnetostriction measurements performed below the T_c reveal a much smaller magnetostriction (maximum strain at most is of the order of 10^{-5} to 10^{-4}), as seen in Fig. 1b. By comparing thermal energy with the magnetic work we find that the thermal energy required to overcome the effect of the applied field corresponds to a system with two spatial degrees of freedom, which correlates with the two-dimensionality of the slabs.
Measurements of the time-dependent magnetization (Fig. 2) as the material was driven through its first order magnetostructural phase transition by an applied magnetic field showed that the transformation dynamics are in accordance with a single activation energy of 4.2 eV in this temperature range (Fig. 3). This result is somewhat surprising, given the complex nature of this particular transformation, where the crystallographic change is coupled with the magnetic ordering.

We have also studied the magnetization and magnetostriction behavior of single-crystal $Tb_5Si_{2.2}Ge_{1.8}$. Magnetization exhibits a strong dependency on the crystallographic direction in which the field is applied,

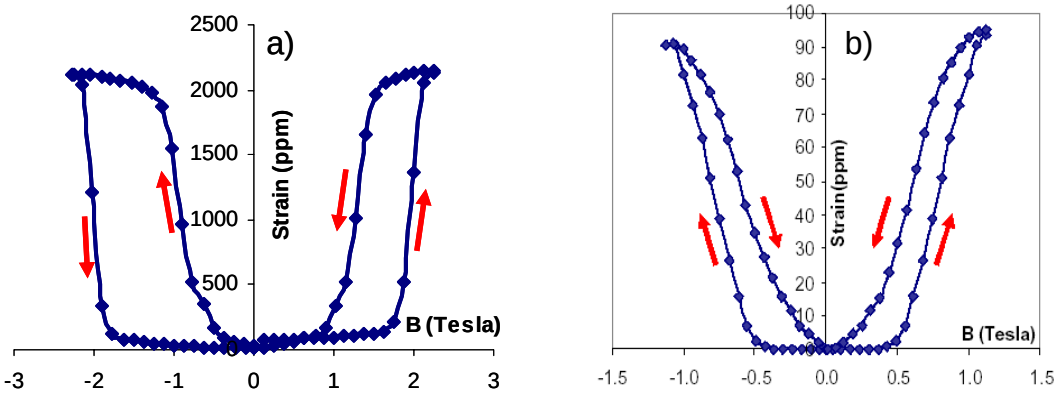


Fig. 1 Giant magnetostriction of $Gd_5Si_2Ge_2$ at a temperature just above the zero magnetic field transition temperature (a) and the same measured just below the zero field transition temperature (b).

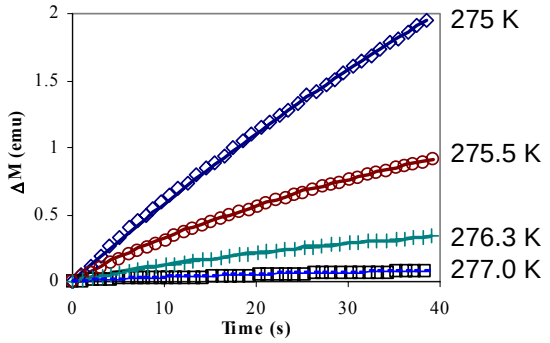


Fig. 2 Measured change in magnetization (symbols) and model calculations (lines) for various T_{sample} above T_c.

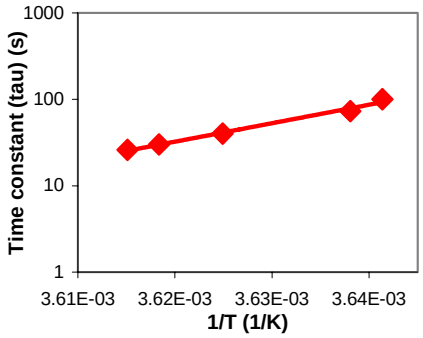


Fig. 3 Log of time constant vs 1/T, confirming the Arrhenius-type behavior with single energy barrier.

showing a stronger magnetic anisotropy than $Gd_5Si_2Ge_2$, leading to the inference that the magnetic and structural transformations in $Tb_5Si_{2.2}Ge_{1.8}$ are not coupled. Therefore its Curie point is not dependent on the applied magnetic field. The magnitude of strain versus magnetic field and slopes of the corresponding curves (Fig. 4) vary through three distinct regions in this material, with the most complex behavior between 98 K and 110 K, which continues until the onset of a paramagnetic phase near 150 K.

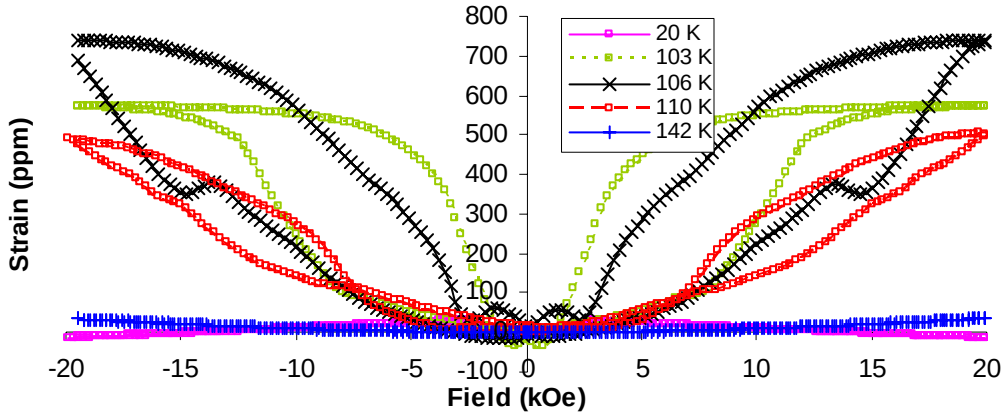


Fig. 4 Magnetostriction of $Tb_5Si_{2.2}Ge_{1.8}$ single crystal, showing some of the complex magnetoelastic behavior.

Impact:

Progress has been made towards understanding the coupled magnetostructural transformation in $Gd_5Si_xGe_{4-x}$ which can be triggered by magnetic field and/or temperature. Similarities and differences in the related $Tb_5Si_xGe_{4-x}$ system have been established. Understanding of the mechanisms involved is critical to further elucidating magnetoelastic behavior near the transition because of the differences in symmetry of the 4*f* electron wave functions of Gd (spherical symmetry) and Tb (non-spherical).

Future Work:

We will systematically study the $Tb_5Si_xGe_{4-x}$ system and other related $R_5Si_xGe_{4-x}$ systems to gain an understanding of the similarities and differences of this alloy family. We will also correlate magnetization and magnetostriction measurements to develop a model of how the crystal reacts to magnetic fields.

Interactions:

Samples were prepared by T.A. Lograsso and D.L. Schlagel (Materials Engineering Physics). Collaboration continues with all the PI's within the Complex and Magnetocaloric Materials Effort. Outside collaborations include M. Pasquale of the Istituto Elettrotecnico Nazionale Galileo Ferraris and L.H. Lewis of Brookhaven National Laboratory.

The Magnetostructural Phase Transition and Anisotropy of the Magnetoresistance in $Gd_5Si_2Ge_2$

Personnel: V.P. Antropov (PI-CMP) and G.D. Samolyuk (Assistant Scientist)

Scope:

The principal aim of this effort is to describe the magnetostructural phase transition and anisotropic change of the magnetoresistance through the transition using the band structure approach. Multiple-scattering formalism of exchange coupling calculation was implemented in frame of the LSDA+U approximation. It was found that the decrease of the exchange coupling through structural deformation leads to a first order magnetostructural phase transition with a large value of $\partial H/\partial T$ and the giant magnetocaloric effect. First principle studies demonstrate that a structural modification is responsible for the anisotropy of the magnetoresistance, and that the latter is due to a significant reduction of electronic velocity in the [100] direction and the anisotropy of electrical conductivity.

Research Highlights:

To avoid local spin density approximation (LSDA) difficulties in case of 4*f* electrons, we applied the traditional multiple scattering theory formalism in LSDA+U. We tested this method for elemental Gd and then studied $Gd_5Si_2Ge_2$ using the tight binding linear muffin tin orbital (TB LMTO) method within the LSDA+U approach with $U = 6.7$ eV and exchange parameter $J = 0.7$. Thermodynamic properties were analyzed within the pair cluster approximation (PCA). Our results demonstrated that in LSDA+U of hcp Gd, the splitting between the occupied and unoccupied 4*f*-states of Gd is increased and effective magnetic exchange becomes positive. The Curie temperature calculated in the mean-field approximation equals 301 K (290 K in PCA), which is in good agreement with the experimental value of 294 K.

The previously described weakening of the "bond strength" in $Gd_5Si_2Ge_2$ is accompanied by a modification of the positions of bonding and anti-bonding states. The position of the anti-bonding *p*-states is lowered below the Fermi level (Fig. 1). In addition, the increase of density of states (DOS) is produced by the nonmagnetic Ge(Si) atoms and is accompanied by a decrease of the magnetic moments of Gd. This modification of the electronic structure leads to a 20% reduction of the effective exchange parameter in the monoclinic (MC) phase. The calculated Curie temperatures are 230 K for the orthorhombic (OR) and 180 K for MC phases. The system undergoes a first order magnetostructural phase transition at $T_m = 206$ K with a nearly 40% reduction of the magnetization. For $T < T_m$, the stable state is the ferromagnetic (FM) OR phase, which at $T = T_m$ it is replaced by the paramagnetic (PM) MC phase. With the increasing magnetic field, the free energy is increased with temperature less sharply than in a zero field and T_m is raised to 223 K when $H = 2$ T. The adiabatic temperature change (Fig. 1) qualitatively reproduces the experimentally observed giant magnetocaloric effect.

Assuming that magnetoresistance (MR) effect is caused by the magnetic-field-induced PM MC→FM OR phase transition and utilizing the current modification of the electronic structure, we calculated MR as a relative change of electronic conductivity in the OR and MC phases using the relaxation time approach. The shift of the anti-bonding states as described above becomes apparent as a significantly decreased dispersion of three bands of the MC-phase. The reduced dispersion of one of these bands is responsible for the peak in the density of states of the MC phase at -0.65 eV, and it leads to the corresponding reduction of electronic velocity, $|v(k)|$, at the Fermi level.

Our calculations also demonstrate that the absolute change of $\langle v_\alpha^2 \rangle$ is practically the same for [010] and [001] directions. This correlates well with the almost negligible change of the interatomic distances along these two crystallographic directions through the structural transition, and the reduction of conductivity occurs because of the increased T1B-T1B (interslab) distance. The large MR in the [010] direction

(perpendicular to the slabs) arises from the smaller $<v_{[010]}^2>$ value compared to the in-slab [100] and [001] directions.

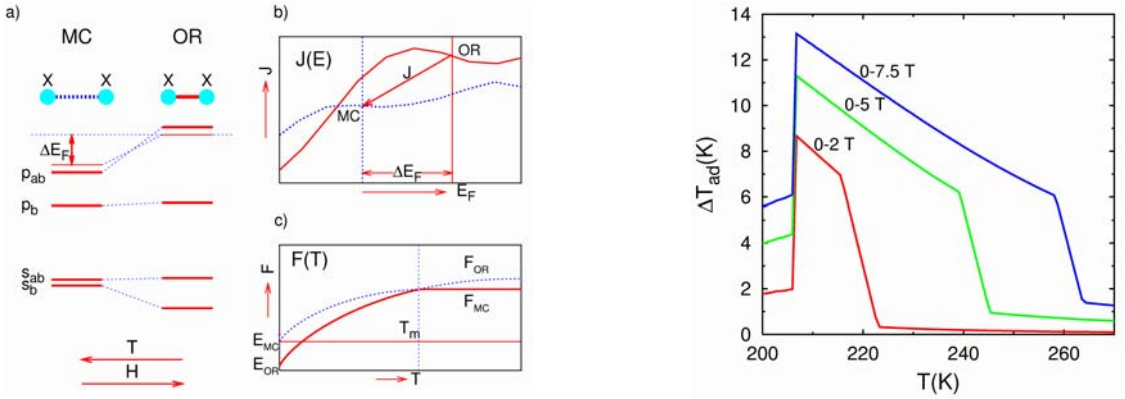


Fig. 1 Left: a) the structure of bonding and anti-bonding states of Ge and/or Si (X) atoms of T1B bonds with the related shift of the E_F; b) the lowering of the effective magnetic exchange parameter, J_0, in the MC phase; c) the free energy, F(T), for both phases. Right: the magnetocaloric effect of $Gd_5Si_2Ge_2$ computed for different magnetic field changes.

The values of MR ratio statistically averaged over possible configurations of Si(Ge) atoms are -26%, -34% and -19% in the [100], [010] and [001] directions, respectively. This result is in agreement with the experimental data.

Impact:

We have proposed a consistent scheme for calculating the magnetic exchange coupling in the frame of multiple scattering theory and the LSDA+U approach. The results for exchange parameters, J_{ij}, are quite sensitive to the potential function parameterization. The T_c value obtained from the calculated J_{ij} in hcp Gd is in good agreement with that obtained from experiment. It was shown that the structural transformation is accompanied by the decrease of *p*-orbital hybridization in T1B – T1B pairs of Ge(Si) atoms. This effect leads to a decrease of the total energy, magnetic moments of the Gd atoms and J_{ij} in the MC phase. The calculated temperature of the magnetostructural phase transition (206 K) is in reasonable agreement with that observed experimentally (270 K). The magnetoresistance calculated from electrical conductivity values along different directions is in qualitative agreement with experiment. The anisotropy of the MR in $Gd_5Si_2Ge_2$ arises from a structural deformation taking place concurrently with a ferromagnetic ordering at T_c because, first, drastic changes in the lattice occur along the [100] direction and, second, the interactions between the slabs along the [010] direction are greatly affected by variability of the T1B – T1B bonds. Combined, these changes in the layered crystal structure of $Gd_5Si_2Ge_2$ result in the smallest MR along the [001] direction.

Future Work:

We continue the development of computer codes for the calculation of the electronic structure and exchange coupling in complex lanthanide-containing alloys with the long-term goal of describing the magnetostructural phase transitions in the range of $Gd_5Si_xGe_{4-x}$ compositions. We will then concentrate on describing similar transitions in $Tb_5Si_xGe_{4-x}$ compounds. Alloys with R = Tb undergo phase transitions that are similar to those found in the $Gd_5Si_xGe_{4-x}$ family but the magnetic and crystallographic phase transformations may be either decoupled or coupled depending on x or hydrostatic pressure.

Interactions:

Multiple PI's in Materials and Engineering Physics Program (K.A. Gschneidner, Jr., V. K. Pecharsky) and Materials Chemistry and Biomolecular Materials (G.J. Miller) Programs.

Magnetic Structures of $R_5Si_xGe_{4-x}$

Personnel: A.I. Goldman (PI), R.J. McQueeney (PI), J.L. Zarestky (PI), C. Stassis (PI), D. Wermeille (Assistant Scientist), V.O. Garlea (Postdoc), A. Kreyssig (Postdoc), B. Sieve, (Postdoc), J.W. Kim (Graduate Student), and L. Tan (Graduate Student)

Scope:

Knowledge of the magnetic and crystal structures is important for the fundamental understanding of the magnetoelastic properties of the $R_5Si_xGe_{4-x}$ compounds. Detailed analyses of the magnetic-martensitic transformations were performed on two different $Tb_5Si_xGe_{4-x}$ stoichiometries with x = 2.2 and x = 2.5 using neutron diffraction measurements requiring large single-crystal and powder samples. The magnetic structure of Gd_5Ge_4, for which the extremely large neutron absorption cross-section of the naturally occurring mixture of Gd isotopes hampers neutron scattering investigations, was studied using x-ray resonant magnetic scattering.

Research Highlights:

Neutron scattering experiments were performed using the HB1A triple axis spectrometer at the High Flux Isotope Reactor at Oak Ridge and the BT-1 instrument at NIST Center for Neutron. Single-crystal elastic neutron scattering measurements were performed over the 8 K - 300 K temperature range, on two different single-crystals of composition $Tb_5Si_{2.2}Ge_{1.8}$. On cooling to approximately 120 K, the $Tb_5Si_{2.2}Ge_{1.8}$ system undergoes a magneto-elastic transition from a high-temperature monoclinic - paramagnetic to a low temperature orthorhombic - ferromagnetic structure. A second magnetic transition occurs at approximately 75 K, without any change in the crystal structure (Fig. 1).

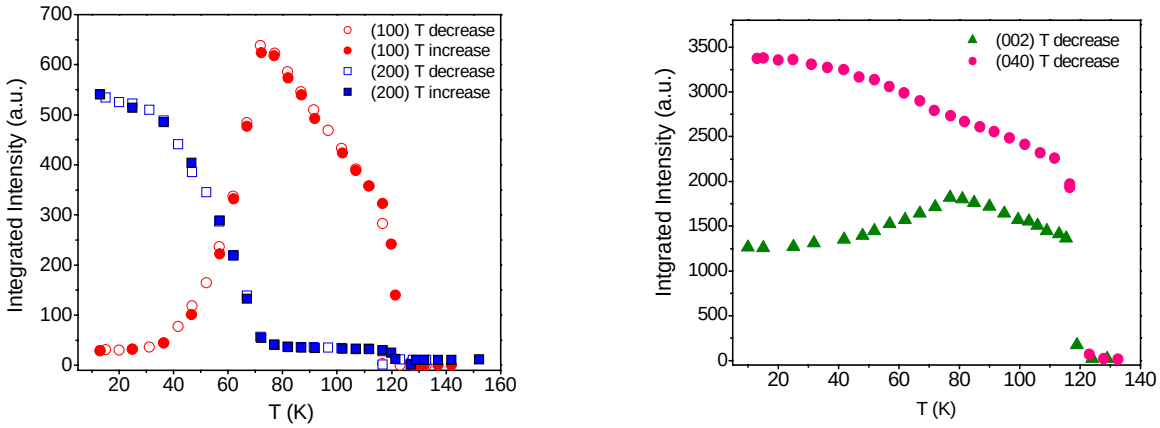


Fig. 1 Evolution in temperature of the integrated intensities of (100) and (200) reflections (left); and (002) and (040) reflections (right) resulting from the single crystal measurements.

The possible magnetic structures, compatible with the *Pnma* symmetry of $Tb_5Ge_{2.2}Si_{1.8}$, were determined by following the representation analysis technique. The resulting models were used to refine the neutron powder diffraction data measured at various temperatures for two different compositions: $Tb_5Si_{2.2}Ge_{1.8}$ and $Tb_5Si_{2.5}Ge_{1.5}$. In the temperature range 120 K to 75 K, the magnetic structure has a net ferromagnetic component along the *a*-axis direction and it was described using a single irreducible representation corresponding to the Shubnikov magnetic space group *Pnm'a'*. The moments are slightly canted with respect to the *a*-axis, while the components along the *b*- and *c*-axes are antiferromagnetically ordered. In the case of $Tb_5Ge_{2.2}Si_{1.8}$, at 75 K, the Tb1, Tb2, Tb3 canting angles with respect to the *a*-axis are 1.3º, 19.6º and 3.1º, respectively. Below 75 K, the magnetic structure consists of a ferromagnetic ordering of the magnetic moments components along *a*- and *c*-axes and an antiferromagnetic arrangement of the *b*-axis moment components. A satisfactory fit of neutron powder data was obtained by mixing the basis vectors of two irreducible representations associated with $P2_12_12_1$ - a subgroup of the *Pnma* space group

symmetry. The refinement results show an increase of the magnetic moment projection along the *c*-axis, and consequently, the canting angles with respect to the *a*-axis direction increase. In the case of $Tb_5Si_{2.2}Ge_{1.8}$, at 4.2 K, they become ~ 35.6º, ~ 47.8º and ~30.5º for Tb1, Tb2 and Tb3, respectively.

We have employed x-ray resonant magnetic scattering (XRMS) to elucidate the details of the magnetic structure of Gd_5Ge_4. The XRMS experiment was performed at the Gd L_2 absorption edge (E=7.934 keV) using the 6ID-B beamline in the MUCAT sector of the Advanced Photon Source. The incident radiation was linearly polarized perpendicular to the vertical scattering plane (**σ** polarized). In this configuration the resonant magnetic scattering, arising from electric dipole transitions (E1, from the 2*p*-to-5*d* states), rotates the plane of linear polarization into the scattering plane (**σ-π** scattering), while charge scattering does not change the polarization of the scattered photons (**σ-σ** scattering). A pyrolytic graphite (0 0 6) single crystal was used as a polarization analyzer in **σ-π** geometry to suppress the charge background relative to the magnetic scattering signal. From azimuthal scans (Fig. 2) and the Q dependence of the magnetic scattering intensities, all three Gd sites in the structure were determined to be in the same magnetic space group *Pnm'a*. The magnetic moments are primarily aligned along the **c** axis and the **c** components of the magnetic moments at the three different sites are equal. The antiferromagnetic structure therefore consists of ferromagnetic Gd-rich slabs that are stacked antiferromagnetically along the **b** direction. The temperature dependence of the magnetic intensity (Fig. 2) shows the Neel temperature (T_N = 125 K).

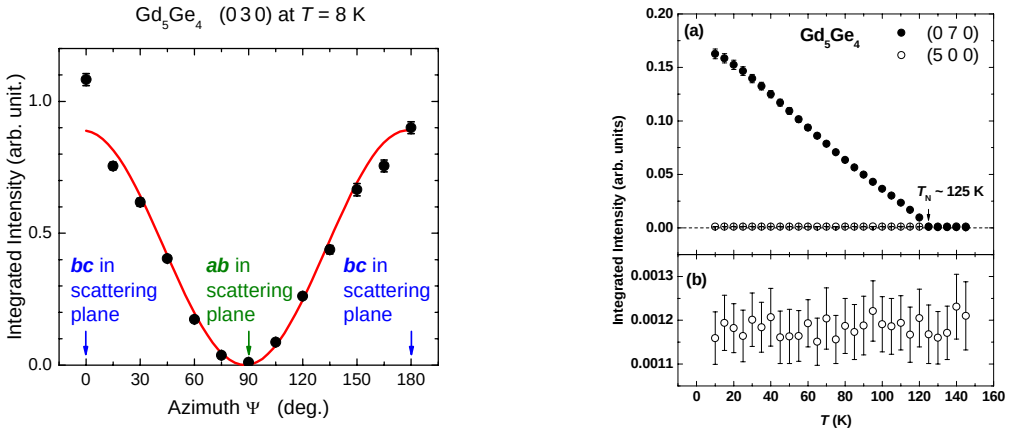


Fig. 2 (Left) The integrated intensity of azimuthal scans of the (0 3 0) magnetic peak normalized by the (0 4 0) charge peak at *T*=8 K. The solid curve represents the variation expected for magnetic moments along the **c**-axis. (Right, a) Integrated intensity of the (0 7 0) and (5 0 0) magnetic peaks measured upon heating the sample, at an azimuth angle of 30°. (Right, b) Integrated intensity of the (5 0 0) resonant peak measured during heating at an azimuth angle of 60°. The (5 0 0) peak is absent in the *Pnm'a* structure.

Impact:

Knowledge of the magnetic structures and their dependence on the crystallographic structure has a direct connection for developing models and understanding of the magnetoelastic coupling and the giant magnetocaloric effect.

Future Work:

We will continue to study magnetic structures for other compositions in the $R_5Si_xGe_{4-x}$ series as a function of temperature and possibly magnetic field. In addition, we suspect that Gd_5Ge_4 samples have significant short-ranged magnetic order above the Neel temperature. We will use a combination of neutron and x-ray magnetic resonant scattering to determine the extent of magnetic short range order.

Interactions:

V.K. Pecharsky, K.A. Gschneidner, Jr., T.A. Lograsso, and D.L. Schlagel (all MEP). Outside collaborations include C.Y. Jones (NIST).

Magnetic Field-induced Polymorphism of Gd_5Ge_4 and the Origin of the Giant Magnetocaloric Effect

Personnel: V.K. Pecharsky (PI), K.A. Gschneidner, Jr. (PI), A.P. Holm (Postdoc), and Y. Mudryk (Postdoc)

Scope:

To image the magnetic field induced structural transformation in Gd_5Ge_4, which occurs below 30 K, by coupling high resolution x-ray powder diffraction with magnetic fields up to 40 kOe; and to demonstrate that the giant magnetocaloric effect, observed in low magnetic fields, arises from amplification of the conventional magnetic entropy change brought about by the entropy change resulting from a concomitant structural change.

Research Highlights:

Gd_5Ge_4 is one of the end members in the series of the $Gd_5Si_xGe_{4-x}$ giant magnetocaloric effect materials. The latter exhibit a factor of 2 to 4 enhancement of the magnetic field induced entropy change between ~20 and ~300 K when compared to the majority of magnetic solids. Gd_5Ge_4 orders antiferromagnetically at ~130 K, and in low magnetic fields the antiferromagnetic state is preserved down to ~2 K. Magnetization, magnetostriction, and electrical resistivity of Gd_5Ge_4 point to a field-induced structural transition (FIST) coupled with a transformation to a collinear ferromagnet below 30 K, but only when the magnetic field exceeds 10 kOe.

X-ray diffraction data were collected on a Rigaku TTRAX rotating anode powder diffractometer (Fig. 1) employing Mo Kα radiation over a wide range of reciprocal space ($\sin\theta/\lambda \leq 0.5$ Å^{-1}). The sample temperature was controlled to within ±0.02 K below 50 K, and better than ±0.05 K above 50 K using a helium flow cryostat coupled with a split-coil superconducting magnet. The magnet provides a uniform 0 to 40 kOe magnetic field around the sample with the magnetic field vector coplanar with the plane of the specimen. The magnetic field was applied after cooling the sample in a zero magnetic field from ~300 K to the measurement temperature. The volume of the examined reciprocal space, the quality, and the resolution of the diffraction data were adequate to determine the changes in the three-dimensional

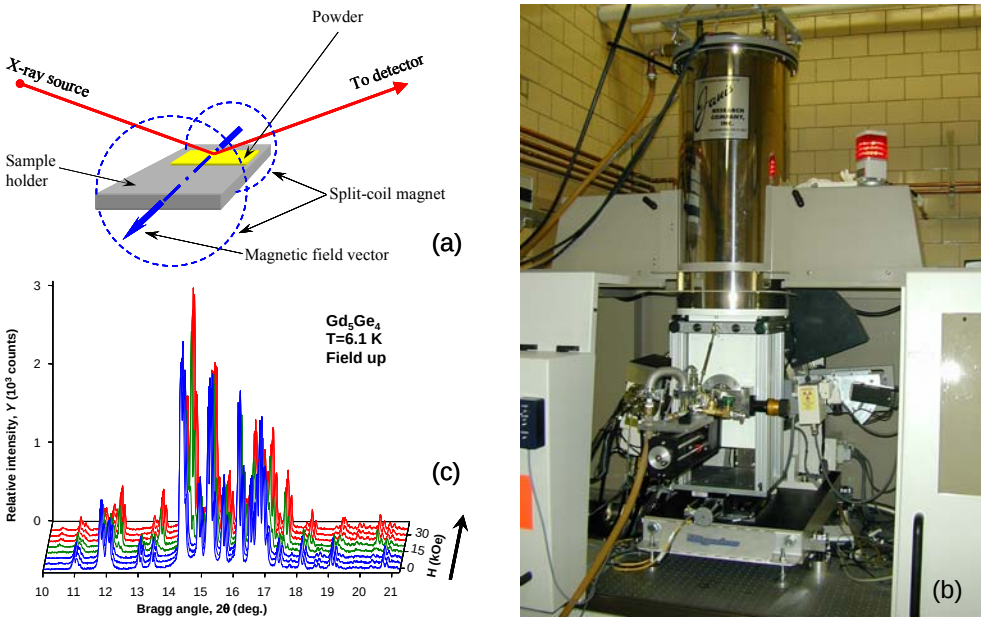


Fig. 1 The principal schematic of how a sample for powder diffraction is magnetized *in situ* (a); the photograph of a powder diffractometer coupled with a continuous flow cryostat and a split coil superconducting magnet (b); and an example of the high resolution powder diffraction data collected while increasing the magnetic field.

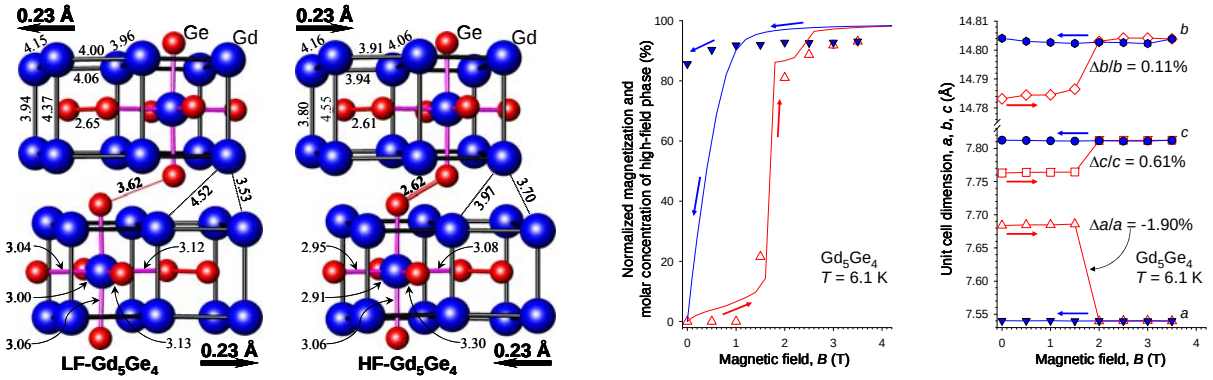


Fig. 2 Magnetic field-induced structural change in Gd_5Ge_4 (left); correlation between magnetic and structural changes together and unit cell dimensions as functions of the magnetic field (right).

distribution of atoms with 0.01 to 0.03 Å accuracy. Phase quantities were determined to within 1 mol. %.

The low magnetic field crystal structure of Gd_5Ge_4 (LF-Gd_5Ge_4) and the high magnetic field polymorphs (HF-Gd_5Ge_4) contain nearly identical layers of atoms arranged in a distinctly different fashion, Fig. 2. The LF-Gd_5Ge_4 and HF-Gd_5Ge_4 relate to one another *via* shear displacements of the neighboring layers by more than 0.2 Å. These relatively large shifts in opposite directions alter numerous interatomic distances and modify interactions among atoms from adjacent layers. The most prominent magnetic field induced change occurs in the interlayer of Ge-Ge bonds. In the LF-Gd_5Ge_4, where the corresponding interatomic distance is $\delta_{Ge\text{-}Ge}$ = 3.62(1) Å, the bonds are weak, but in the HF-Gd_5Ge_4 they become much stronger due to a 1 Å contraction [$\delta_{Ge\text{-}Ge}$ = 2.62(1) Å].

The FIST observed in Gd_5Ge_4 correlates with the magnetization behavior measured at the same temperatures. As seen in Fig. 2, the fraction of the HF-Gd_5Ge_4 formed at 6.1 K by increasing magnetic field, follows the initial magnetization path. Consistent with the macroscopic magnetism, the system preserves the HF-Gd_5Ge_4 structure, whose concentration is only slightly reduced from 93 to 86 % when the magnetic field is lowered from 35 kOe to 0.

The large magnetic field induced phase volume and chemical bonding changes, observed in Gd_5Ge_4, show that the giant MCE is achieved due to the concomitant change of the entropy during the structural transformation. As a result, the observed giant MCE is the sum of the conventional magnetic entropy-driven process and the difference in the entropies of the two crystallographic modifications.

Impact:

The nature of the magnetic field induced structural changes in Gd_5Ge_4 has been established with the atomic resolution allowing for improved first principle calculations. Our research indicates that new and advanced magnetocaloric materials should exist in solid systems where extensive structural changes are coupled with ferromagnetic ordering, and therefore, can be triggered by a magnetic field.

Future Work:

In-situ structural determination in other $R_5Si_xGe_{4-x}$ systems, such as $Tb_5Si_xGe_{4-x}$, where magnetic and structural transformations can be either decoupled or coupled as function of x and the decoupling is measured by a few Kelivn. Later, examine the $Er_5Si_xGe_{4-x}$ system, especially, Er_5Si_4 where the structural transition is located far away from the magnetic ordering (the two are nearly 200 K apart) and where there is an apparent effect of the magnetic field on the structural transition temperature.

Interactions:

This work is in collaboration with multiple PI's in the Complex and Magnetocaloric Materials effort. We have also initiated a collaboration with C. Nelson (Brookhaven).